Dynamic and static behaviors of CH4 and CO2 in small and large cavities of hydrate

doi: 10.1016/j.molstruc.2012.10.015

Dynamic and static behaviors

of CH_4 and CO_2 in small and large cavities of hydrate

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We investigated the static structures and dynamic behaviors for guest molecules (CH_4 and CO_2) in small and large cavities which are composed of 12 pentagonal faces of 20 water molecules (5^{12}), and 12 pentagonal and 2 hexagonal faces of 24 water molecules ($5^{12}6^2$), respectively, by B3LYP/6-311++G(d,p) level calculations in GAUSSIAN 09, and using quantum molecular dynamics (QMD) (NVT MD with semiempirical MO PM3 method). For the static calculations, the guest CO_2 and CH_4 molecules are around at the center of small and large cavities with weak H-bond formations of H-O-H$\cdots$$O_2C$ and $H_2O\cdots H_4C$ van der Waals interaction systems. Calculated carbon NMR chemical shifts of the CH_4 in the gas-state and in the small and large cavities reflected the C-13 experimental tendency, while the calculated carbon NMR chemical shifts of the CO_2 in the three states almost correspond to the experimental value in the gas-state. For QMD calculations, we used a cluster model containing 73 water molecules, and examined dynamic behavior of guest molecules in the shell cluster model of 39 water molecules which own small and large cavities. The dynamic behavior of guest molecules are simulated from the trajectory distribution of molecular center of the mass due to the translational motion, and also analyzed using librational motions of guest molecules in the cavities.

Keyword: Gas hydrate, guest molecule, quantum chemical and QMD calculations,

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Introduction

Gas hydrates are known to have various structures that depend on the sizes of guest molecule and condition under their existence [1, 2]. Major structures are sI, sII, and sH, especially sI, which includes small guest molecules e.g. CH_4, C_2H_6, and CO_2, is most popular in nature. In sI, there are two types of small and large cavities. The small cavity is pentagonal dodecahedra (5^{12}), while the large cavity is tetradecanhedra ($5^{12}6^2$) having two opposite hexagonal faces and twelve pentagonal faces (in Fig. 1).

For the gas hydrates from industrial potentials, we can arrange three useful reasons; (i) CH_4 hydrate as a new energy resource; since abundant volumes of CH_4 exist in the form of hydrate in nature. (ii) CO_2 Hydrate as the reduction of green house effect; substitution of CH_4 in methane hydrate with CO_2 , because CO_2 is stably enclosed in hydrate cavity [3]. (iii) CH_4 Hydrate as a transportation material instead of natural gas one; since methane hydrate can store huge volume of CH_4 stably. We, then, think that it is often important to obtain information on unique dynamic and static behaviors of the hydrates from a fundamental viewpoint as well as for such industrial background.

Quantum chemical calculation and molecular dynamics (MD) methods have important roles for the theoretical study of the dynamic and static behaviors of the hydrates, and it has been used to investigate the hydrate nucleation and growth process [4-8], and to find out the effective hydrates inhibitors to decrease the pipeline blockages. In some useful studies with first principles MD method, Ikeda and coworker [9] investigated the structural, dynamical, and electronic properties of methane hydrate under pressure and at room temperature. Tse [10] inquired into the stretching vibrations of methane in the small and large cavity of sI clathrate hydrate closely. Grossman et al. [11] showed that water molecules surrounding hydrophobic solute CH_4 are

oriented in a similar fashion, and that the driving force for this orientation is the water-water interaction rather than the water-solute interaction. As described in our previous work [12], we focused that CH_4 forms weak hydrogen bonds with water molecules and through this interaction, and CH_4 lessened motion of water. This weak interaction might also play an important role in the nucleation and growth process for CH_4 hydrate.

In the present study, we aim to provide the information on static and dynamic behaviors of guest molecules (CH_4 and CO_2) in our hydrate model cluster from the nanometer-scopic local viewpoint. In quantum chemical calculations, carbon NMR chemical shifts of CO_2 and CH_4 in gas, and in the two cluster cavities are calculated in comparison of the experimental values. For quantum molecular dynamics (QMD) calculations, we use hybrid (semiempirical MO PM3)-MD method in which interatomic interactions are evaluated in semiempirical MO method, in order to visualize the motions for guest molecules in both small and large cages.

Computational Methods

a) Quantum chemical calculation

The initial geometric structures of CO_2, CH_4, $20H_2O$ as a small cavity, and $24H_2O$ as a large cavity were optimized at a semiempirical PM3 MO method [13]. We performed the second geometry-optimization with the B3LYP [14, 15]/6-311++G(d,p) basis level method in GAUSSIAN 09 program [16] by using the cartesian coordination of the initial geometry structures. In both geometry-optimizations, we fixed the coordinates of all oxygen atoms for framework of the small and large cavities using the neutron diffraction data [17] (at 150K). The bond lengths, bond angles and dihedral angles of all hydrogen atoms for two cavities were optimized in the calculation. For the other geometry-optimization with the

B3LYP/6-311++G(d,p) basis level, we calculated the gas(CH_4 and CO_2)-cluster model systems in which the carbon of guest molecules are fixed and free in the center of the two cavities.

We used the B3LYP/6-311++G(d,p) basis level method in order to obtain the carbon NMR chemical shielding tensors of CO_2, CH_4, and the gas-cluster (CH_4 and CO_2) model systems . The NMR chemical shielding tensors were calculated in the coupled perturbed Hatree-Fock (CPHF) method with the gauge invariant atomic orbital (GIAO) [18]. The calculated chemical shift for ^{13}C is defined by

$$\Delta\sigma = \sigma_{quest} - \sigma_{ref} \quad , \qquad (1)$$

where σ_{quest} and σ_{ref} are the chemical shielding constants in question and the reference. The calculated chemical shift is given relative to the reference, tetramethylsilane (TMS). For TMS, we also used B3LYP/6-311++G(d,p) basis level method, and calculated the shielding constants in the CPHF method with the GIAO.

All quantum chemical calculations were performed in GAUSSIAN 09 program.

b) QMD calculation

For our QMD calculation, we used in a cluster model containing 73 water molecules as a part of sI hydrate. In the case of the cluster model molecule, we divided into two groups; (a) the first shell (in Fig. 2) is composed of 39 water molecules which own small (5^{12}) and large ($5^{12}6^2$) cavities jointly, (b) the second shell contains other 34 water molecules which surround the first shell. During QMD simulation, the water molecules in the second shell were considered only in the force calculation due to the MO method, and their positions were fixed in the trajectory calculations.

The NVT-MD simulations were performed in a cluster model structure containing 73 water molecules. The two guest molecules were placed in the first shell model in Fig. 2: One was in the

small cavity and the other in the large cavity. We used the velocity Verlet algorithm [19] for the integration of equation of motion with time step of 0.5 fs. The QMD simulations for 8000 times iterations of 4ps were then performed for subsequent analysis. The potential energy is given from the interatomic force function as the differential calculus of the potential energy by quantum chemical calculation. The force function is evaluated automatically from the semiempirical PM3 MO calculations of the cluster model containing 73 water molecules. We set the temperature of the systems at 270K with a Berendsen thermostat [20] and kept it by the velocity scaling method [21, 22].

Results and Discussion

a) Static structure and C13 NMR chemical shift from quantum chemical calculation

In order to obtain the local structural information and electronic state about the guest molecules in the small and large cavities, Fig. 3 {a) ~ d)} and {e) ~ h)} showed the guest molecules (CO_2 and CH_4), respectively, at the geometry-optimization with the carbon of the guest molecules fixed and free in the center of two cavities. In the figure {a) ~ d)} and {e) ~ h)}, all guest CO_2 and CH_4 molecules are seen to exist around at the center of small and large cavities.

For the figure {a) ~ d)}, we examined the weak H-bond possibility for (H-O-H$\cdots O_2$C) van der Waals interaction system in the small and large cavities from the two center bond-order analysis. Then, for the CO_2 molecules in the two cavities in Fig. 3 {a) ~ d)}, the H-bond energy of H-O-H$\cdots O_2$C system amounts to be in maximum energy values of 2.4 and 1.9 kcal/mol (for the H-bond distances of 2.6 and 3.1 Å) in the small and large cavities, respectively.

In the case of Fig. 3 {e) - h)} in carbons of methane molecules fixed and free in the center of the small and large cavities, we also confirmed that there are the weak H-bonds for

($H_2O\cdots H\text{-}CH_3$) van der Waals interaction systems in the two cavities from the two center bond-order analysis. Thus, the methane protons were found-out to have weak H-bonding with oxygen atoms of cluster water molecules in maximum energy values of 1.3 and 1.0 kcal/mol (for the H-bond distances of 2.7 and 3.1 Å) in the small and large cavities, respectively.

In Table 1, we showed the ^{13}C NMR chemical shielding constants for the guest molecules by B3LYP/6-311++G(d,p) level calculations. The calculated ^{13}C NMR chemical shielding constants and the shift values referred to TMS were performed in types of the CO_2 and CH_4 molecules in gas, small and large cavities with the guest carbon fixed and free in the center of the cavities. For the CO_2 molecules, the calculated carbon NMR chemical shifts in the three states almost correspond to the experimental value in the gas-state [23]. In the case of CH_4 molecules with the C fixed and free in the center of small and large cavities, we also obtained similar values of the calculated chemical shielding constants. The calculated chemical shifts correspond well to the experimental results in gas, small and large cavities [24]. Therefore, we are able to predict that guest CH_4 molecules in the solid-high-resolution NMR measurements exist around at the center of small and large cavities with the weak H-bond formation.

b) Dynamic behavior of guest molecules from MD calculation

It is interesting to discuss the local dynamic behavior of the guests in the hydrate cages. We, then, analyze the translational and librational motions of the CH_4 and CO_2 molecules in the cavities in Fig. 2.

(i)Translational motions of the guest molecule in the cages

We examined the dynamic property of CH_4 and CO_2 molecules in the small and large cavities from the trajectory distribution of molecular center of the mass due to the translational motions. Fig. 4 shows the simulated results of the trajectories for CO_2 and CH_4, respectively. In the large and small cavities, CO_2 molecule moves around the centers of cavities. On the other hand, CH_4

also runs around the center in the small cavity, while, in the large cavity, it seems to stay at some position where is distant from the center.

As showed in the static structural analysis, the result tells us that CH_4 exists around at the center of large cavity. In the earlier experimental and theoretical studies [10, 25, 26], they also described that CH_4 and CO_2 molecules in the crystalline hydrate cavities moves around the center of the large cavity. Thus, we have to examine the reason why 'CH_4 exists at some position in the large cavity' using the NVT-MD with PM3 MO method. Then, we tried to calculate the CH_4-large cavity-cluster model system in which the carbon of CH_4 molecule is free in the center of the large cavity using the semiempirical MO PM3 method. In the geometry-optimization, we also fixed the coordinates of all oxygen atoms for framework of the large cavity using the neutron diffraction data [17] (at 150K). The bond lengths, bond angles and dihedral angles of all hydrogen atoms for the cavity were optimized in the calculation. We obtained the optimization result in Fig. 5 where CH_4 exists at some position where is distant from the center. Here, we determined to exclude that the result of the CH_4 in the large cavity using QMD with PM3 method is an exceptional specific interaction case.

(ii) Librational motions for the guest molecule in the cavities

In the small cavity, the motion of CO_2 molecule is recognized to keep at the initial position, since the small cavity is no room size. In the case of the large cavity, we know it has some preferable orientation to perform the librational motions. Then, we expected to find out the preferable orientation by using the variable angle between the two double bond molecular axis of CO_2 and the symmetry axis of large cavity, as shown in Fig. 6. In Fig. 7, we showed the angle dependency with time between the two axes for librational motions of CO_2 molecule. It can be seen from the figure that the librational motion of CO_2 is restricted in equatorial plane of the large cavity, as the angle is apt to approach to 90°. The result corresponds well to the study [27] for

crystalline CO_2 hydrate.

For the librational motion of the CH_4 molecule in the cvities, we consider the librational motion of the CH_4 molecule only in the small cavity. In order to clarify the nature of the librational motion in the small cavity, we tried to analyze the motion property from the correlation function, $Corr(t) = \mathbf{u}(t) \cdot \mathbf{u}(0)$, where unit vector $\mathbf{u}(t)$ is along each C-H bond of the CH_4 molecule at time *t*, since the highly symmetric shape of the methane is considered that mainly two of the vibrational modes interact directly with infrared light. We can see the time dependency of the correlation function from Fig. 8 that CH_4 molecule rotates almost freely in the small cage.

Conclusions

We studied the static and dynamic behaviors for guest molecules (CH_4 and CO_2) in small and large water cluster cavities by B3LYP/6-311++G(d,p) level calculations in GAUSSIAN 09, and using NVT MD with semiempirical MO PM3 method.

For the static calculations, the guest CO_2 and CH_4 molecules are around at the center of small and large cavities with the weak H-bond formation of (H-O-H$\cdots$O=C=O and $H_2O\cdots$H-CH_3) van der Waals interaction system. The H-bond energy of H-O-H$\cdots O_2C$ system amounts to be in maximum energy values of 2.4 and 1.9 kcal/mol (for the H-bond distances of 2.6 and 3.1 Å) in the small and large cavities, respectively. The methane protons were found-out to have weak H-bonding with oxygen atoms of cluster water molecules in maximum energy values of 1.3 and 1.0 kcal/mol (for the H-bond distances of 2.7 and 3.1 Å) in the small and large cavities, respectively.

For NMR carbon chemical shifts, the calculated carbon NMR chemical shifts of the CO_2 molecule in the three states almost correspond to the experimental value in the gas-state. The calculated carbon chemical shifts of CH_4 correspond well to the experimental C-13 results in gas, small and large cavities. Therefore, we are able to predict that guest CH_4 molecules in the solid-high-resolution NMR measurements exist around at the center of small and large cavities with the weak H-bond formation.

In QMD calculations with semiempirical PM3 method, we examined the dynamic properties from the trajectory distribution of molecular center of the mass due to the translational motion in the two cavities. In the large and small cages, CO_2 molecule moves around the centers of cages, while, in the case of CH_4, we it seems to stay at some position where are distant from the center of the large cage. In the latter case of the result for the CH_4 in large cavity, we excluded it as the exceptional specific interaction system. We can accept that CH_4 molecules are around at the center of large cavity due to the B3LYP/&-311++G(g,p) level calculation in GAUSSIAN.

We also analyzed the dynamic behaviors from librational motions of CO_2 molecule in the cavities. The librational motion of CO_2 is restricted in equatorial plane of the large cage, as the angle is apt to approach to 90°. The result corresponds well to the experimental study for crystalline CO_2 hydrate. It can be seen from the time dependency of the correlation function, ($Corr(t) = \mathbf{u}(t) \cdot \mathbf{u}(0)$, where unit vector $\mathbf{u}(t)$ is along each C-H bond of the CH_4 molecule at time t), that CH_4 molecule rotates almost freely in the small cage.

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Table 1. Calculated ^{13}C NMR chemical shielding constants of CO_2 and CH_4 in gas, small and large cavities, and the chemical shifts referred to TMS

	^{13}C chemical shielding constants			^{13}C chemical shifts	
				calc	exper
gas state	σ^{dia}	σ^{para}	σ^{total}	$\Delta\sigma$	$\Delta\sigma$
B3LYP/6-311++G(d,p) (with guest carbon fixed in the center of the cavity)					
CO_2 in gas	263.61	-210.33	53.28	125.72	124.2
CO_2 in small cavity	289.72	-236.06	53.66	125.34	
CO_2 in large cavity	284.23	-230.73	53.50	125.50	
TMS	249.50	-70.50	179.00	0.00	0.00
CH_4 in gas	247.25	-56.84	190.41	-11.41	-7.00
CH_4 in small cavity	269.59	-83.76	185.83	-6.83	-2.84
CH_4 in large cavity	257.49	-70.06	187.43	-8.43	-5.71
B3LYP/6-311++G(d,p) (with guest carbon free in the center of the cavity)					
CO_2 in gas	263.61	-210.33	53.28	125.72	124.2
CO_2 in small cavity	289.89	-236.19	53.70	125.30	
CO_2in large cavity	283.90	-230.64	53.26	125.74	
TMS	249.50	-70.50	179.00	0.00	0.00
CH_4 in gas	247.25	-56.84	190.41	-11.41	-7.00
CH_4 in small cavity	269.54	-83.70	185.84	-6.84	-2.84
CH_4 in large cavity	257.71	-70.26	187.45	-8.45	-5.71

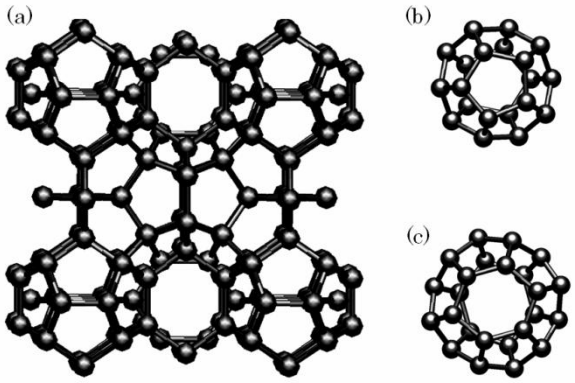


Fig. 1. Crystal structures (a) sI hydrate (b) small cage (c)large cage, respectively.

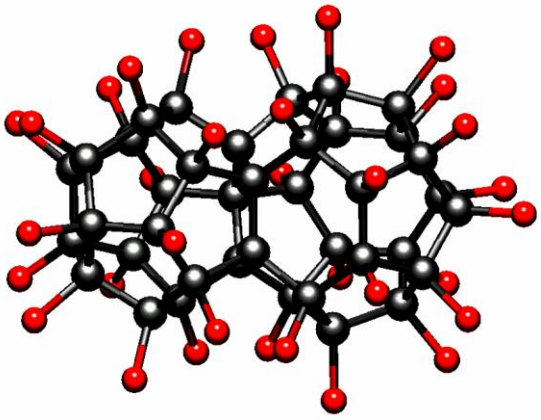
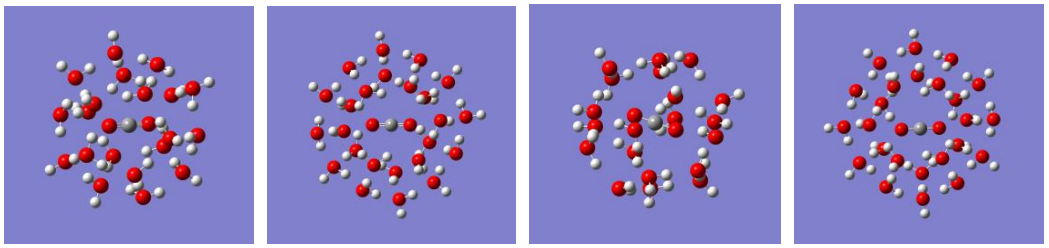


Fig. 2. Model structure of small hydrate cluster. Balls and sticks express the water oxygens and hydrogen bond networks respectively

a)CO_2 (fixed C) in S-cage b) CO_2 (fixed C) in L-cage c) CO_2 in S-cage d) CO_2 in L-cage



e) CH_4 (fixed C) in S-cage f) CH_4 (fixed C) in L-cage g) CH_4 in S-cage h) CH_4 in L-cage

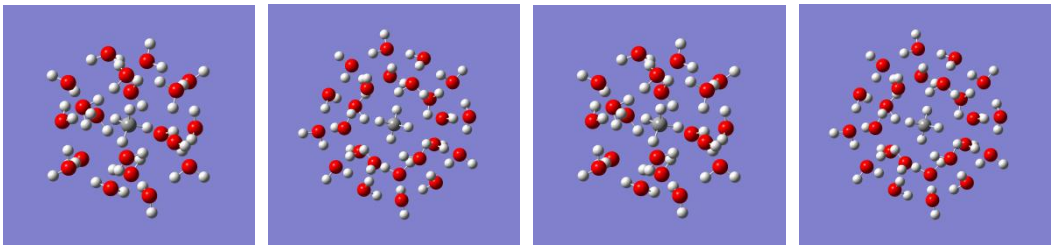
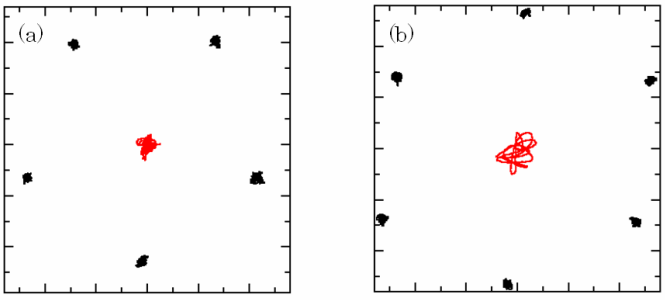
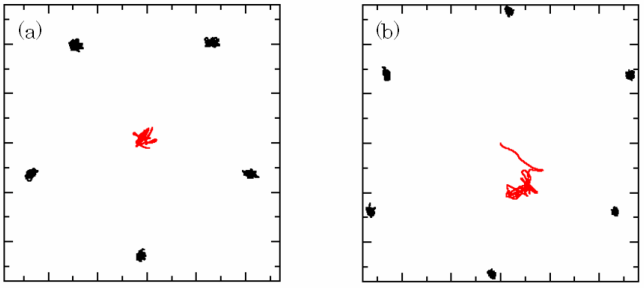


Fig. 3. CO_2 and CH_4 molecules in small and large cages with and without C fixed guest molecules at the geometry-optimization.



a) CO_2 in small cage b) CO_2 in large cage



c) CH_4 in small cage d) CH_4 in large cage

Fig. 4. Trajectory distribution of molecular center of mass of CO_2, and CH_4 in the small and large cages;

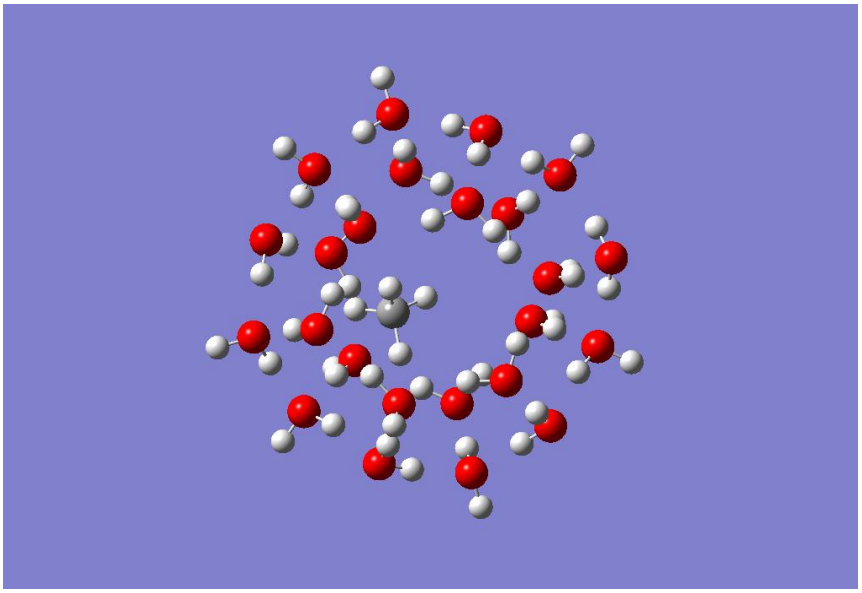


Fig.5 CH_4 in large cavity using semiempirical MO PM3 method

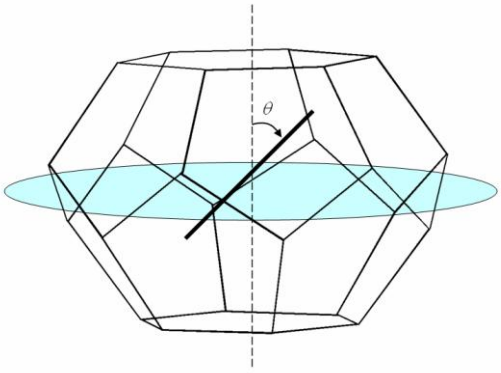


Fig. 6. Angle (θ) between the molecular axis of CO_2 and the symmetry axis of large cage.

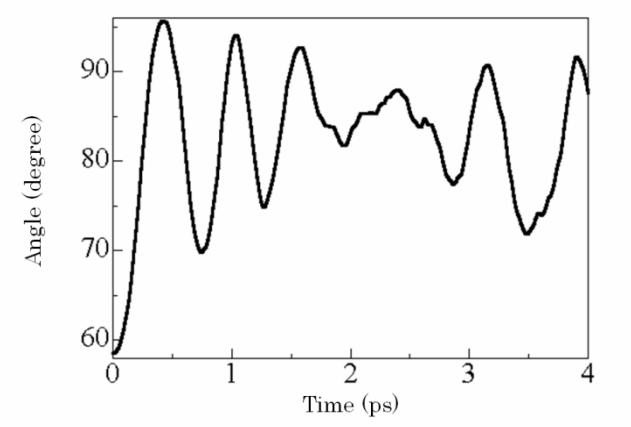


Fig. 7. Angle dependency with time between the two axes for librations of CO_2 molecule

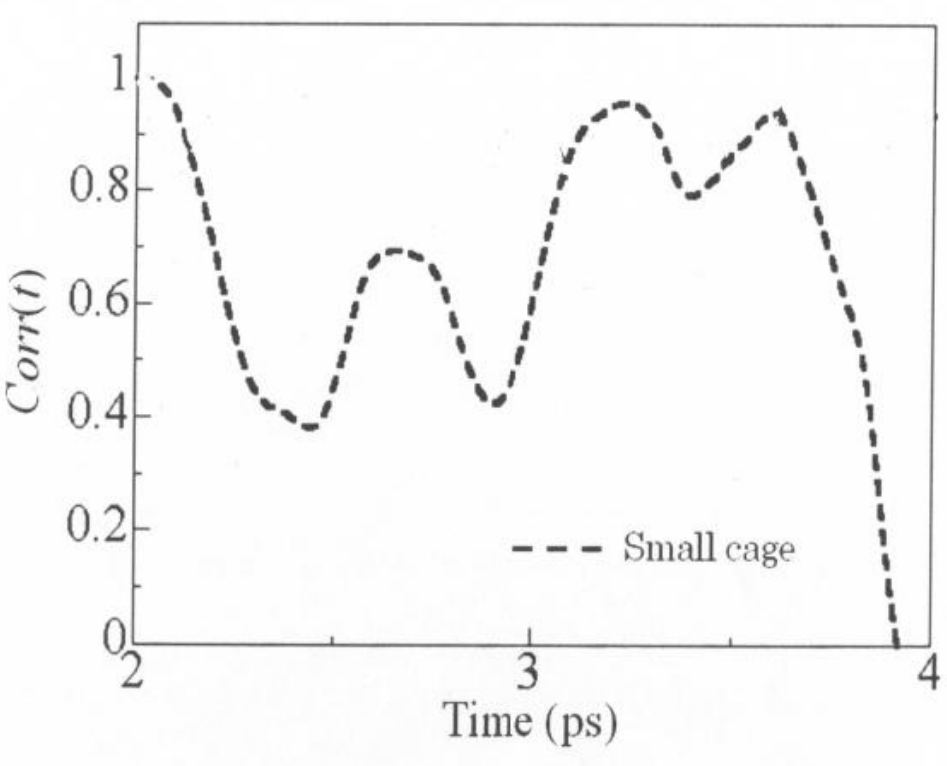


Fig. 8 Correlation of the unit vector, which is along C-H bond of CH_4.